

PATENT SPECIFICATION

552,682

Application Date: Oct. 15, 1941. No. 13288/41.

Complete Specification Left: Oct. 15, 1942.

Complete Specification Accepted: April 20, 1943.



PROVISIONAL SPECIFICATION

Improvements in or relating to the Shredding of Cellulosic Materials

ERRATA

SPECIFICATION No. 552,682.

Page 2, line 65, for "cut,," read "cut,"
Page 3, line 37, for "cellulose,," read

"cellulose,," after "exceed" insert
"25° C."

Page 4, line 38, for "Refyerring" read
"Referring"

Page 4, line 107, for "therefore" read
"therefor"

THE PATENT OFFICE,
September 27th, 1943.

25 ticular reference to sheets and films of
regenerated cellulose (which are water-
sensitive), since it is in this respect that
the invention displays its greatest advan-
age, it is to be understood that the inven-
tion is applicable to sheets, films, tubes,
30 filaments and yarns of water-sensitive
cellulosic materials generally, including
sheets, films, tubes, filaments and yarns
cast from lowly substituted cellulose
ethers, cellulose esters and cellulose ether-
35 esters, such as glycol cellulose, methyl
cellulose, cellulose glycollic acid and
cellulose phthalic acid.

The manufacture of a sheet or film by
continuously regenerating cellulose from
40 viscose commonly involves forcing the
viscose through a shaped orifice into a
coagulating bath to form a coherent web,
which freshly coagulated web is then
promptly regenerated, washed, desul-
45 phured, bleached, softened (glycerinated)
and dried. During the manufacture of
regenerated cellulose sheets and films, and
the production of articles therefrom,
there is formed waste sheet or film
60 material, the satisfactory use or disposal
of which has heretofore presented
difficulties.

[Price 1/-]

whereby the dimensions of the cellulosic
materials are reduced rapidly, with at the
same time low heat-development in the
mass and with economy of power-con-
sumption.

To this end the invention comprises a
process for the shredding of water-
sensitive cellulosic materials, which com-
prises treating the cellulosic materials so
as to cause the latter to absorb water sub-
stantially throughout the mass of the
materials, whereby the strength and
toughness of the latter are considerably
reduced, and then tearing or grinding or
cutting by mechanical means the treated
cellulosic materials to form pieces thereof
of the desired dimensions.

Preferably the treatment of the cellu-
losic materials so as to cause the latter to
absorb water is such that the cellulosic
materials thereby become substantially
saturated with water.

The invention includes shredded cellu-
losic materials produced by the process in
accordance with the invention.

As a result of the treatment of the
cellulosic materials so as to cause the
latter to absorb water throughout the
mass of the materials whereby the

Price 5s. 6d.

PATENT SPECIFICATION



Application Date: Oct. 15, 1941. No. 13288/41.

552.682

Complete Specification Left: Oct. 15, 1942.

Complete Specification Accepted: April 20, 1943.

PROVISIONAL SPECIFICATION

Improvements in or relating to the Shredding of Cellulosic Materials

We, BRITISH CELLOPHANE LIMITED, a British Company, of Bath Road, Bridgwater, Somerset, GEORGE SAMUEL HEAVEN, a British Subject, of "Croftside", Chedzoy, Bridgwater, Somerset, and ERNEST BUTLER, a British Subject, of 51, Quantock Road, Bridgwater, Somerset, do hereby declare the nature of this invention to be as follows:—

10 This invention comprises improvements in or relating to the shredding of cellulosic materials, and is concerned more particularly with the shredding of water-sensitive cellulosic materials in the form of sheets, films, tubes, filaments, and

15 yarns. Water-sensitive cellulosic materials are characterised in that they absorb water when they are brought into contact with water or water-vapour; in so doing they tend to change their dimensions.

20 While for convenience the invention will be described hereinafter with particular reference to sheets and films of regenerated cellulose (which are water-sensitive), since it is in this respect that the invention displays its greatest advantage, it is to be understood that the invention is applicable to sheets, films, tubes, 25 filaments and yarns of water-sensitive cellulosic materials generally, including sheets, films, tubes, filaments and yarns cast from lowly substituted cellulose ethers, cellulose esters and cellulose ether-esters, such as glycol cellulose, methyl cellulose, cellulose glycollic acid and cellulose phthalic acid.

30 The manufacture of a sheet or film by continuously regenerating cellulose from viscose commonly involves forcing the viscose through a shaped orifice into a coagulating bath to form a coherent web, which freshly coagulated web is then promptly regenerated, washed, desulphured, bleached, softened (glycerinated) and dried. During the manufacture of regenerated cellulose sheets and films, and the production of articles therefrom, there is formed waste sheet or film 35 material, the satisfactory use or disposal of which has heretofore presented difficulties.

[Price 1/-]

Attempts to shred on a practical scale by mechanical means a mass of dry regenerated cellulose sheets or films to produce small pieces thereof have failed for various reasons, among which may be mentioned the difficulty of cutting and grinding the sheets and films owing to the great strength and toughness of the latter, the great heat-development in the mass, the clogging of the moving parts of the machine by the sheets or films and the wrapping of the latter around the moving parts, with the result that the rate of disintegration of the mass of sheet or film is slow, heat-development is frequently dangerously high and power-consumption is excessive.

One of the objects of the present invention is to provide a process for the shredding of water-sensitive cellulosic materials, in the form of a mass of sheets, films, tubes, filaments or yarns, by grinding and cutting by mechanical means, whereby the dimensions of the cellulosic materials are reduced rapidly, with at the same time low heat-development in the mass and with economy of power-consumption.

To this end the invention comprises a process for the shredding of water-sensitive cellulosic materials, which comprises treating the cellulosic materials so as to cause the latter to absorb water substantially throughout the mass of the materials, whereby the strength and toughness of the latter are considerably reduced, and then tearing or grinding or cutting by mechanical means the treated cellulosic materials to form pieces thereof of the desired dimensions.

Preferably the treatment of the cellulosic materials so as to cause the latter to absorb water is such that the cellulosic materials thereby become substantially saturated with water.

The invention includes shredded cellulosic materials produced by the process in accordance with the invention.

As a result of the treatment of the cellulosic materials so as to cause the latter to absorb water throughout the mass of the materials whereby the

Price 5s. 6d.

strength and toughness of the latter are considerably reduced, the cellulosic materials are readily torn, ground or cut by mechanical means of known types, clogging of the moving parts of the machines by the materials is avoided, power-consumption is low and heat-development is slight. Thus by the process of the invention cellulosic materials may readily be reduced to small pieces, resembling flakes, of substantially uniform size.

There will now be described, by way of example, one way in which the process of the invention may be carried out:—

Dry, glycerine-softened, plain regenerated cellulose sheets, including small trimmings and larger pieces of waste sheet measuring up to 44" x 60", of various commercial thicknesses, were made up into batches each weighing 50 lbs. Each batch was treated in turn in a washing machine, which was of the known horizontal cylindrical type, the inner barrel of which, into which the batch was loaded, was made of perforated sheet material, and was caused by means of mechanism to rotate in directions alternately clockwise and anti-clockwise. The sheet material was washed with water at from 20°—40° C. until the material was free from glycerine. From the wash-waters containing glycerine in dilute aqueous solution, glycerine may be recovered by known methods either as pure glycerine or as a concentrated aqueous glycerine solution.

The treated sheet material was removed from the washing machine and was charged, still as a complete batch into a rotary hydro-extractor of the known type, in which it was whizzed so as to remove the free water. The batch of treated material, after whizzing, was in the substantially saturated state, and weighed 97½ lbs.

The batch of substantially saturated material was placed in a jacketted shredding machine of a known type, fitted with rotatable blades, and was ground by driving the blades, the directions of rotation of the blades being reversed after successive periods of 10 minutes. A flow of cooled calcium chloride was maintained around the jacket surrounding the shredding machine, so that during the grinding operation the temperature of the batches did not rise above 25° C. Grinding was continued in dealing with the various batches for periods of from 1—4½ hours, for each batch, dependent upon the state

of division of the original sheets of the batch. The material was ground and cut, by the action of the shredding machine, into small irregular-shaped pieces, resembling flakes, having a maximum dimension of about ¾".

The shredded material removed from the shredding machine may be dried, or for other purposes may be used in the saturated condition. If, by weighing before shredding, the batch is found to have lost water, e.g. during storage, water equal in weight to that lost may be added to the batch during the early stages of the shredding operation, the subsequent shredding and mixing treatments causing a uniform distribution of the added water, whereby a final water-containing shredded product of standard and uniform composition is obtained.

Moistureproof regenerated cellulose sheet, comprising for example a base sheet of regenerated cellulose coated with a surface coating composition comprising a cellulosic base such as cellulose ether or ester, a gum or a resin, a wax or the like and preferably a plasticiser, as described in British Patent No. 283,109, may also be used, but the surface coating composition should be removed from the base sheet before treatment of the sheet in the shredding machine. This may be done by soaking the moistureproof regenerated cellulose sheet in water or dilute aqueous caustic soda, containing for example about 1.0% NaOH, at a temperature not in excess of 25° C., until the surface coating composition floats off, or may be readily removed by scraping, from the base sheet. The base sheet, thus freed from the surface coating composition, is then washed, whizzed and treated in the shredding machine in the way described above.

Small proportions, up to about 10%, of cellulosic materials, such as wood pulp, which are not water-sensitive, may be shredded together with water-sensitive cellulosic materials by the process in accordance with the invention.

Shredded cellulosic materials, produced by the process in accordance with the invention may be used with advantage in the production of viscose by the process described in the co-pending Application No. 13287/41 (Serial No. 552,681).

Dated this 15th day of October, 1941.
BOULT, WADE & TENNANT,
111 & 112, Hatton Garden,
London, E.C.1.
Chartered Patent Agents.

COMPLETE SPECIFICATION

Improvements in or relating to the Shredding of Water-Sensitive
Non-Fibrous Cellulosic Materials

We, BRITISH CELLOPHANE LIMITED, a British Company, of Bath Road, Bridgwater, Somerset, GEORGE SAMUEL HEAVEN, a British Subject, of "Croftside", Chedzoy, Bridgwater, Somerset, and ERNEST BUTLER, a British Subject, of 51, Quantock Road, Bridgwater, Somerset, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention comprises improvements in or relating to the shredding of water-sensitive non-fibrous cellulosic materials.

Water-sensitive cellulosic materials are characterised in that they absorb water when they are brought into contact with water or water-vapour; in so doing they tend to change their dimensions.

While for convenience the invention will be described hereinafter with particular reference to sheets and films of regenerated cellulose produced from viscose, (which are water-sensitive and non-fibrous), since it is in this respect that the invention displays its greatest advantages, it is to be understood that the invention is also applicable to sheets, films, tubes, filaments and yarns of water-sensitive non-fibrous cellulosic materials generally, including sheets, films, tubes, filaments and yards of regenerated cellulose solution, lowly substituted cellulose ethers, such as glycol cellulose, methyl cellulose and ethyl cellulose, lowly substituted cellulose esters such as lowly acetylated cellulose, and lowly substituted cellulose ether-esters, such as lowly acetylated lowly substituted ethyl cellulose, produced by casting or spinning from an aqueous cellulosic solution or dispersion; and the expression "water-sensitive non-fibrous cellulosic material" as used in this specification and claims is to be understood as including such regenerated cellulosic materials. On the other hand, highly etherified cellulose and highly esterified cellulose, for example ordinary cellulose acetate containing about 54% acetyl, are not water-sensitive for the purpose of this invention.

The manufacture of a sheet or film by continuously regenerating cellulose from viscose commonly involves forcing the viscose through a shaped orifice into a coagulating bath to form a coherent web,

which freshly coagulated web is then promptly regenerated, washed, desulphured, bleached, softened (glycerinated) and dried. During the manufacture of regenerated cellulose sheets and films, and the production of articles therefrom, there is formed waste sheet or film material, the satisfactory use or disposal of which has heretofore presented difficulties.

Hitherto attempts to shred, on a practical scale by mechanical means, a mass of dry regenerated cellulose sheets or films to produce small pieces thereof have failed for various reasons, among which may be mentioned the difficulty of cutting and grinding the sheets and films owing to the great strength and toughness of the latter, the great heat-development in the mass, the clogging of the moving parts of the machine by the sheets or films and the wrapping of the latter around the moving parts; with the result that the rate of disintegration of the mass of sheet or film is slow, heat-development is frequently dangerously high and power-consumption is excessive.

One of the objects of the present invention is to provide a process for the shredding of water-sensitive non-fibrous cellulosic materials, in the form of a mass of sheets, films, tubes, filaments or yarns, by tearing or grinding or cutting by mechanical means, whereby the dimensions of the said sheets, films, tubes, filaments or yarns are rapidly reduced with, at the same time, low heat-development in the mass and with economy of power-consumption.

To this end the invention comprises a process for the shredding of "water-sensitive non-fibrous cellulosic material", which process comprises first treating the cellulosic material so as to cause the latter to absorb water substantially throughout the mass of the material, whereby the strength and toughness of the latter are considerably reduced; and thereafter tearing or grinding or cutting by mechanical means the treated cellulosic material to form pieces thereof of the desired dimensions.

Preferably the treatment of the cellulosic material so as to cause the latter to absorb water is such that the cellulosic material thereby becomes substantially saturated with water. During the tearing or grinding or cutting, the treated cellulosic material may be cooled, prefer-

ably to such a degree that the temperature of the latter does not exceed.

The invention includes shredded water-sensitive non-fibrous cellulosic material 5 when produced by the process in accordance with the invention.

As a result of the treatment of the cellulosic material, whereby it is caused to absorb water throughout its mass, the 10 cellulosic material is readily torn, ground or cut by mechanical means of known types, clogging of the moving parts of the machines by the material is avoided, power-consumption is low and 15 heat-development is slight. Thus, by the process of the invention, regenerated cellulose sheets and films may readily be reduced to small pieces, resembling flakes, of substantially uniform size.

20 The treated cellulosic material may be torn, ground or cut in apparatus of known types. One known form of apparatus that has been found specially suitable for the shredding of the treated 25 cellulosic material is shown by way of example, in the accompanying drawings, wherein:—

Figure 1 illustrates, mainly diagrammatically, one form of the apparatus 30 shown in a sectional end elevation;

Figure 2 is a plan view of the parts shown in Figure 1, and

Figures 3, 4 and 5 are sectional views of details of the apparatus.

35 Like reference numerals indicate like parts in the several Figures of the drawings.

Referring to the drawings, the shredding apparatus comprises a massive 40 cast-steel body, having inner walls 10 and outer walls 11, the space 12 between the inner walls and outer walls acting as a jacket serving for the circulation of cooling liquid. The inner container, 45 the sides of which are constituted by the inner walls 10, may conveniently be 6 feet long, 5 feet wide and 4 feet deep, open at the top and curved at the base, as shown. The inside surface of the curved 50 base is covered, over the rising saddle parts 13 thereof, with a large plurality of sharply pointed raised pyramidal teeth, approximately $\frac{3}{16}$ inch high, with the remainder of the inside surface of the 55 curved base and also the inside surface of the inner walls 10 smooth and devoid of teeth.

Rotatably mounted in bearings carried by opposite end-walls of the apparatus are 60 four trunnions 14, 15, 16 and 17 on which are rigidly mounted massive cast-steel arms 18, 19, 20 and 21. The arms 18 and 19 carry rigidly mounted therein the two more or less helically curved blades 22 65 and 23, and the arms 20 and 21 carry the

two more or less helically curved blades 24 and 25, the blades 22, 23, 24 and 25 being likewise massive and of cast steel. Each of the curved blades 22, 23, 24 and 25 bears on its outer side, indicated by 70 26 (see Figure 1) in respect of the outer edge of the blade 22, and over the entire length thereof, a large plurality of strong steel teeth 27, each about $\frac{1}{2}$ inch high, the teeth being uniformly spaced about $\frac{1}{2}$ 75 inch apart, as shown in Figure 3 and Figure 4, which show diagrammatically a short length of one of the said curved blades in longitudinal cross-section and in transverse cross-section respectively. 80 Figure 5 shows diagrammatically a transverse cross-section of one of the teeth 27 on a larger scale. The clearance between the teeth 27 and the teeth with which the inside surface of the curved base is 85 covered, over the rising saddle parts 13 thereof, is about 0.03 inch. The pairs of blades, 22 and 23, and 24 and 25, respectively, are rotated by any convenient source of power (not shown) and are inter- 90 connected by intermeshing gear-wheels 28 and 29, mounted on the trunnions 15 and 17 respectively, whereby the pairs of blades are caused to rotate in opposite directions and at different speeds. The 95 rotating blades serve, with the aid of the teeth 27 in co-operation with the teeth with which the inside of the curved base is covered, over the rising saddle parts 13 thereof, to tear, grind, or cut the treated 100 cellulosic materials into smaller pieces and these pieces are thoroughly and continuously intermixed.

Cooling liquid is passed through the jacket space 12 the inlet for such cooling 105 liquid being indicated at 30 and the outlet therefore at 31. The rate of flow of liquid through the jacket space 12 is controlled by means of an adjustable valve, diagrammatically 110 indicated at 33, arranged in the outlet 31, and an adjustable valve, diagrammatically indicated at 32, arranged in the inlet 30.

At its upper side, marginal and 115 inclined inwardly directed plates 34 are provided and the whole apparatus is mounted so that it is capable of being rotated, about its longitudinal axis (i.e. about an axis parallel with the axes of the 120 shredding blades) sufficiently far to bring it into a more convenient position for removal of the shredded material. The means for so mounting the apparatus are, however, not illustrated, as they may take 125 any desired form.

The following are examples of the process according to the invention, wherein the treated cellulosic material is 130 shredded in this apparatus.

EXAMPLE I.

Dry, glycerine-softened, plain regenerated cellulose sheet, including small trimmings and larger pieces of waste sheet measuring up to 44 inches x 60 inches, of various commercial thicknesses, were made up into batches each weighing 50 lbs. Each batch was treated in turn in a washing machine, which was of the known horizontal cylindrical type, the inner barrel of which, into which the batch was loaded, was made of perforated sheet material, and was caused by means of mechanism to rotate in directions alternately clockwise and anticlockwise. The sheet material was washed with cold water, which extracted the glycerine therefrom, and the washing was continued until the material was free from glycerine. The temperature of the washing water was 20° C.

In dealing with other batches, the temperature of washing water lay within the range between 20° C. and 40° C.; temperatures in excess of about 40° C. should preferably be avoided.

From the wash-waters containing glycerine in dilute aqueous solution, glycerine may be recovered, either in the form of pure glycerine or in the form of a concentrated aqueous solution thereof, by known methods.

The sheet material, washed free from glycerine, was removed from the washing machine and was charged, still as a complete batch, into a rotary hydro-extractor of the known type, in which it was whizzed so as to remove the free water. The batch of treated cellulosic material, after whizzing, was in the substantially saturated state, and weighed 97½ lbs.

The batch of substantially saturated material, together with five similar batches of like substantially saturated material, was placed in the jacketted shredding apparatus, described above with references to Figures 1 to 5, and the whole of the treated material was shredded by rotating the blades, the directions of rotation of the blades being reversed after successive periods of 10 minutes. A flow of aqueous calcium chloride solution, cooled to about 7° C., was maintained through the space between the outside of the body and the inside of the jacket, so that during the shredding operation the temperature of the material that was being shredded did not rise above 25° C. Shredding was continued for 2½ hours. The treated cellulosic material was thus shredded by tearing, grinding and cutting into small irregular-shaped pieces, resembling flakes, having a maximum dimension of about ¼ inch.

In dealing with other batches, it was found that shredding had to be continued for periods of from 1 hour to 4½ hours, dependent upon the nature and quality of the original sheet material, and upon the state of division of the sheets of the batch.

EXAMPLE II.

175 lbs. of clean, waste viscose rayon in the form of skeins, cakes and miscellaneous lengths of fibre, normally obtained as reject material in the manufacture of rayon by the viscose process, were steeped in water, having a temperature of about 20° C., for about 15 minutes, whereupon the rayon material, having been thoroughly wetted with water, was removed from the water and was charged into a rotary hydro-extractor of the known type, in which it was whizzed so as to remove the free water. The batch of treated cellulosic material, after whizzing, had a thoroughly damp feel, but showed no free surface water, and was apparently in the substantially water-saturated state. The batch of treated cellulosic material, after whizzing, weighed 390 lbs.

The batch of substantially saturated material was placed in the jacketted shredding apparatus, and the whole of the treated material was shredded by rotating the blades, the directions of rotation of the blades being reversed after successive periods of 15 minutes. A flow of aqueous calcium chloride solution, cooled to about 5° C., was maintained through the space between the outside of the body and the inside of the jacket, so that during the shredding operation the temperature of the material that was being shredded did not rise to above 20° C. Shredding was continued for 2½ hours. The treated cellulosic material was thus shredded, by tearing, grinding and cutting, by the action of the shredding apparatus, into small pieces. The average fibre-length of the finished shredded material was found to be 0.14 cm. The finished shredded material was very fluffy.

In all cases the shredded material removed from the shredding apparatus may be dried, or for other purposes may be used in the saturated condition. If, by weighing before shredding, a batch is found to have lost weight, e.g. by evaporation of water during storage, additional water in predetermined amount, e.g. in amount equal in weight to that lost, may be added to the batch during the early stages of the shredding operation, the subsequent shredding and mixing treatments causing a uniform distribution of the added water, whereby a final water-

containing shredded product of standard and uniform composition is obtained.

Moistureproof regenerated cellulose sheet material, comprising for example a base sheet of regenerated cellulose coated with a surface coating composition comprising a cellulosic base such as cellulose ether or ester, a gum or a resin, a wax or the like and preferably a plasticiser, as described in British Patent Specification No. 283,109, may also be used, but the surface coating composition should be removed from the base sheet before treatment of the sheet material in the shredding apparatus. This may be done by soaking the moistureproof regenerated cellulose sheet material in water or dilute aqueous caustic soda, containing for example about 1.0% NaOH, at a temperature not in excess of 25° C., until the surface coating composition floats off, or may be readily removed by scraping, from the base sheet. The base sheet, thus freed from the surface coating composition, is then washed, whizzed and treated in the shredding apparatus as described above.

Shredded regenerated cellulose materials, produced by the process in accordance with the invention, may be used with advantage in the production of viscose by the process described in the copending Application No. 13287/41.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the shredding of "water-sensitive non-fibrous cellulosic material", which process comprises first treating the cellulosic material so as to cause the latter to absorb water substantially throughout the mass of the material, whereby the strength and toughness of the latter are considerably reduced, and thereafter tearing or grinding or cutting by mechanical means the treated cellulosic material to form pieces thereof of the desired dimensions.

2. A process as claimed in Claim 1, in which the "water-sensitive non-fibrous cellulosic material" is in the form of sheets, films, tubes, filaments or yarns.

3. A process as claimed in Claim 1 or

Claim 2, in which the "water-sensitive non-fibrous cellulosic material" is regenerated cellulose produced from viscose or from cuprammonium cellulose solution.

4. A process as claimed in Claim 1 or Claim 2, in which the "water-sensitive non-fibrous cellulosic material" is lowly substituted cellulose ether, or lowly substituted cellulose ester, or lowly substituted cellulose ether ester produced by casting or spinning from an aqueous cellulosic solution or dispersion.

5. A process as claimed in any of the preceding Claims, in which the treatment of the cellulosic material so as to cause the latter to absorb water is such that the cellulosic material thereby becomes substantially saturated with water.

6. A process as claimed in any one of the preceding Claims, in which additional water is added in predetermined amount to the cellulosic material during the early stages of the tearing or grinding or cutting thereof.

7. A process as claimed in any one of the preceding Claims, in which the cellulosic material is subjected, prior to tearing or grinding or cutting, to a purifying treatment, whereby non-cellulosic constituents, such as softener or surface coating composition, are removed therefrom.

8. A process as claimed in Claim 7, in which the purifying treatment is carried out simultaneously with the treatment to cause the cellulosic material to absorb water substantially throughout the mass of the material.

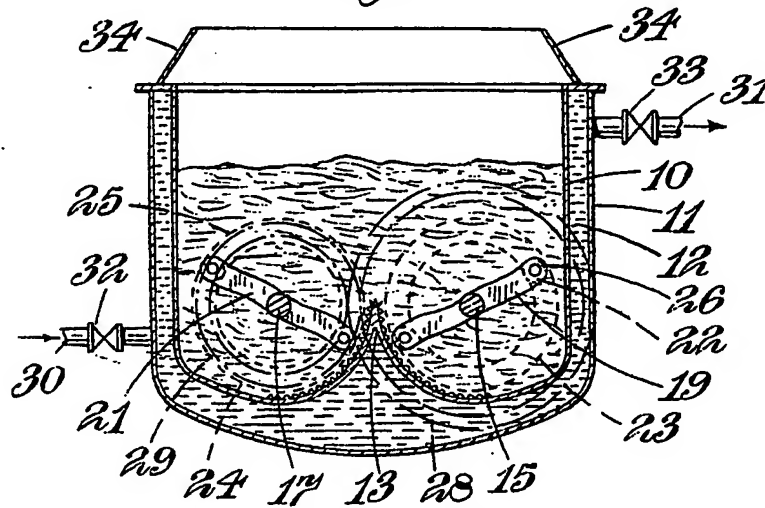
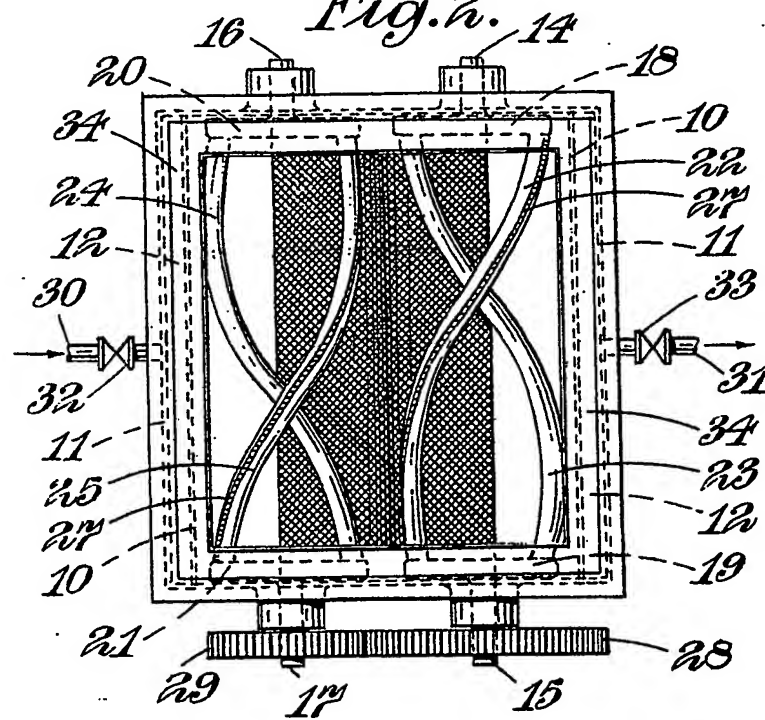
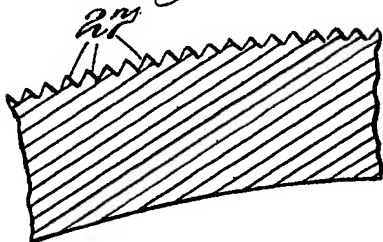
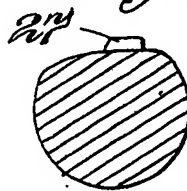
9. A process as claimed in any of the preceding Claims, in which the shredded cellulosic material is subsequently dried.

10. A process as claimed in Claim 1, and substantially as hereinbefore described with reference to Example I, or Example II.

11. Shredded "water-sensitive non-fibrous cellulosic materials" when produced by the process as claimed in any one of the preceding Claims.

Dated this 15th day of October, 1942.

BOULT, WADE & TENNANT,
111/112, Hatton Garden, London, E.C.1.
Chartered Patent Agents.

Fig. 1.*Fig. 2.**Fig. 3.**Fig. 4.**Fig. 5.*